



Direct Reaction Cell ICP-MS vs. XRF: Which is the Superior Technique for the Analysis of Water-Soluble and Total Elements in Fine Particulate Matter?

Presented at the NETL PM2.5 and Electricity Power Generation:
Recent Findings and Implications

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Steubenville Comprehensive Air Monitoring Program (SCAMP)

- **Funding Agencies:**
 - **Indoor Air and Personal Exposure:** Ohio Coal Development Office, Electric Power Research Institute, American Petroleum Institute, American Iron and Steel Institute, National Mining Association, National Institute of Environmental Health Sciences
 - **Outdoor Ambient Air Program:** U.S. Department of Energy, U.S. EPA
- **Participating Groups:**
 - **Indoor Air and Personal Exposure:** CONSOL Energy R&D, Harvard School of Public Health, Franciscan University of Steubenville,
 - **Outdoor Ambient Air Program:** CONSOL Energy R&D, Ohio University, Franciscan University of Steubenville, St. Vincent College, Wheeling Jesuit University



Program Design

- **Outdoor Ambient Air**
 - Continuous
 - May 2000 - May 2002
 - A central site in Steubenville surrounded by 4 remote sites
- **Indoor and Personal Exposure**
 - Four 10-week Intensives
 - Summer and Fall of 2000: Older Cardiovascular Patients
 - Winter and Summer of 2001: Early School Age Children



Program Goals

- Provide a comprehensive database for use in epidemiological studies, long-range transport studies, and for regulatory issues.

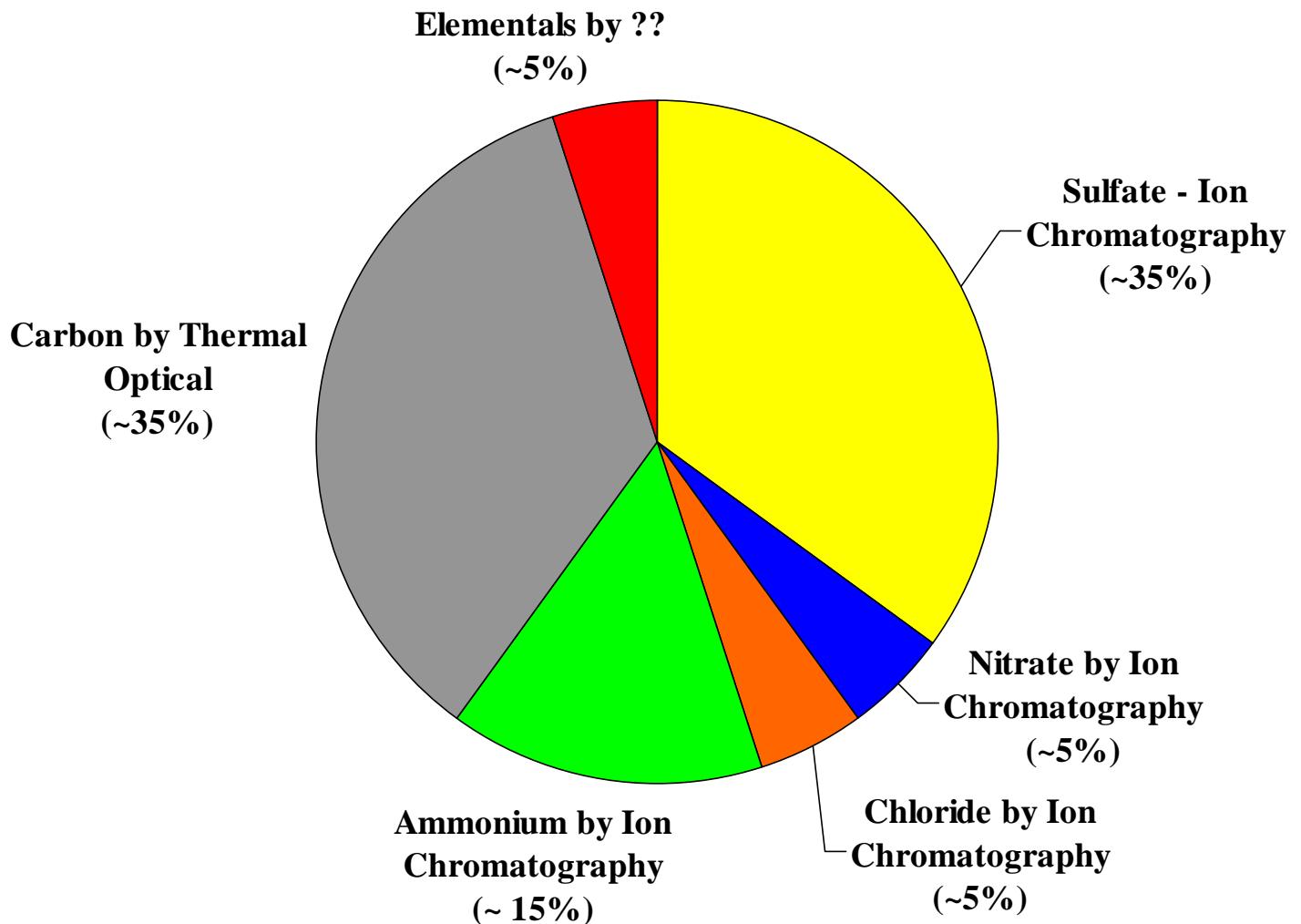


State Implementation Plans (SIPS)

- **Control Strategies for Fine Particulate**
 - Relative contribution from a source or class of sources
 - Composition and relationship to adverse health effects
- **White House Office of Management & Budget advised USEPA to refocus its fine particulate research**
 - “If research can identify those particles most responsible for health risks, it may be possible to design controls that do more for public health and cost the economy less than would occur through policies that assume all particles are equally toxic.”



Analytical Methods





Elements of Interest

- 21 elements
- Ca, K, Al, Cr, Mn, Se, Fe, Na, Mg, Si, Ti, V, Cu, Co, Ni, Zn, As, Cd, Sn, Ba, Pb



Why are these Elements So Important?

- Elements provide a profile of a source or sources
- Transitional elements and species have been the focus of much of the health debate
 - e.g. V, Zn, and Fe



X-ray Fluorescence (XRF) vs. Conventional ICP-MS

- **X-ray Fluorescence**
 - **Advantages**
 - Non-destructive
 - Dissolution not necessary
 - Good precision for major elements
 - **Disadvantages**
 - Sensitivity
 - Limited applications at masses < 20 amu
- **Conventional ICP-MS**
 - **Advantages**
 - Sensitivity-ppt
 - Speed
 - Widely Applicable
 - **Disadvantages**
 - Destructive
 - Dissolution required
 - Molecular interferences

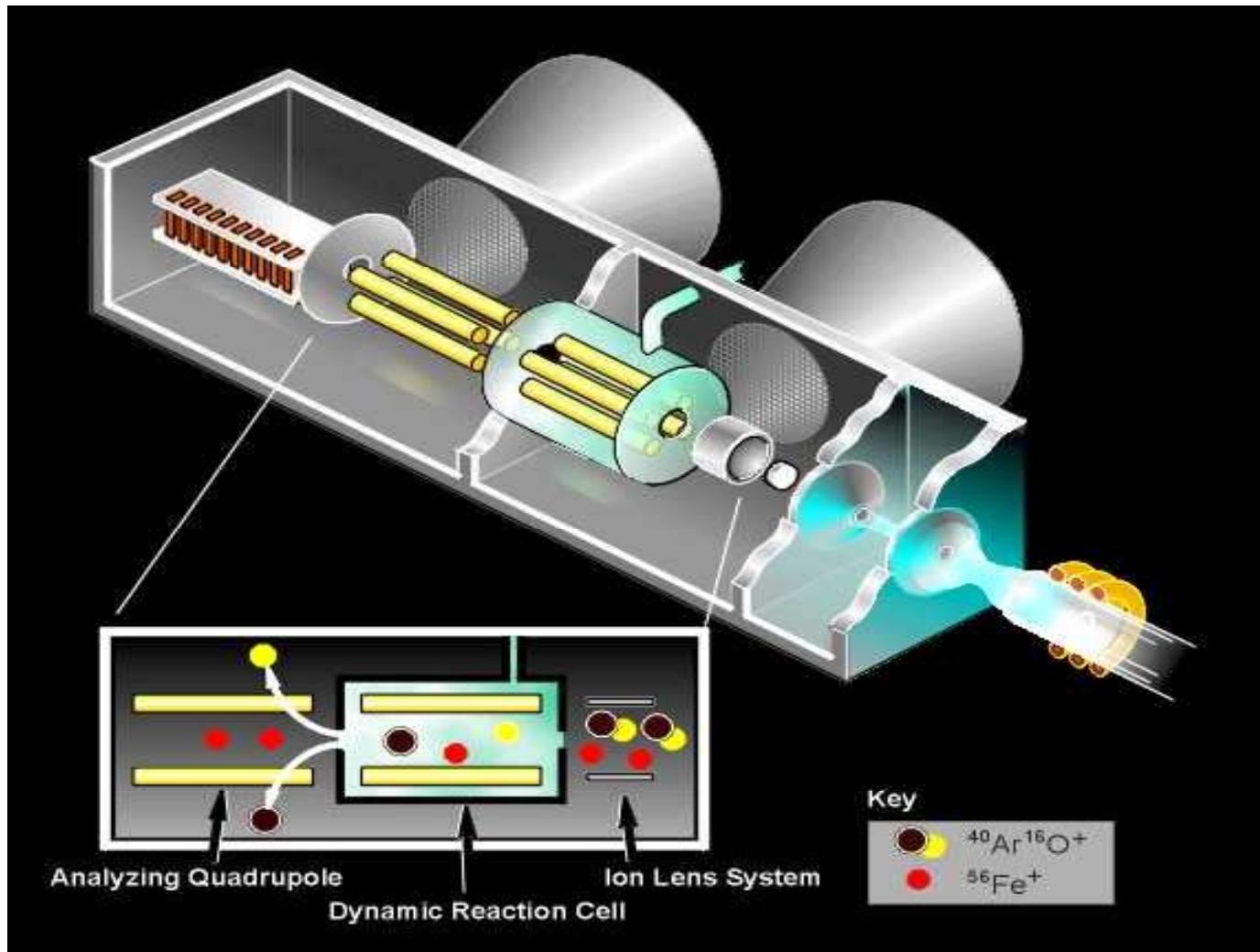


Molecular Interferences

Isotope Molecular Interferences

– ^{28}Si	– $^{14}\text{N}^{14}\text{N}$, $^{12}\text{C}^{16}\text{O}$
– ^{39}K	– ^{38}ArH
– ^{40}Ca	– ^{40}Ar
– ^{51}V	– $^{35}\text{Cl}^{16}\text{O}$, ^{37}ClN
– ^{52}Cr	– $^{40}\text{Ar}^{12}\text{C}$, $^{36}\text{Ar}^{16}\text{O}$, $^{35}\text{Cl}^{16}\text{OH}$
– ^{56}Fe	– $^{40}\text{Ar}^{16}\text{O}$
– ^{75}As	– $^{40}\text{Ar}^{35}\text{Cl}$
– ^{80}Se	– $^{40}\text{Ar}^{40}\text{Ar}$

Direct Reaction Cell ICP-MS (DRC ICP-MS)



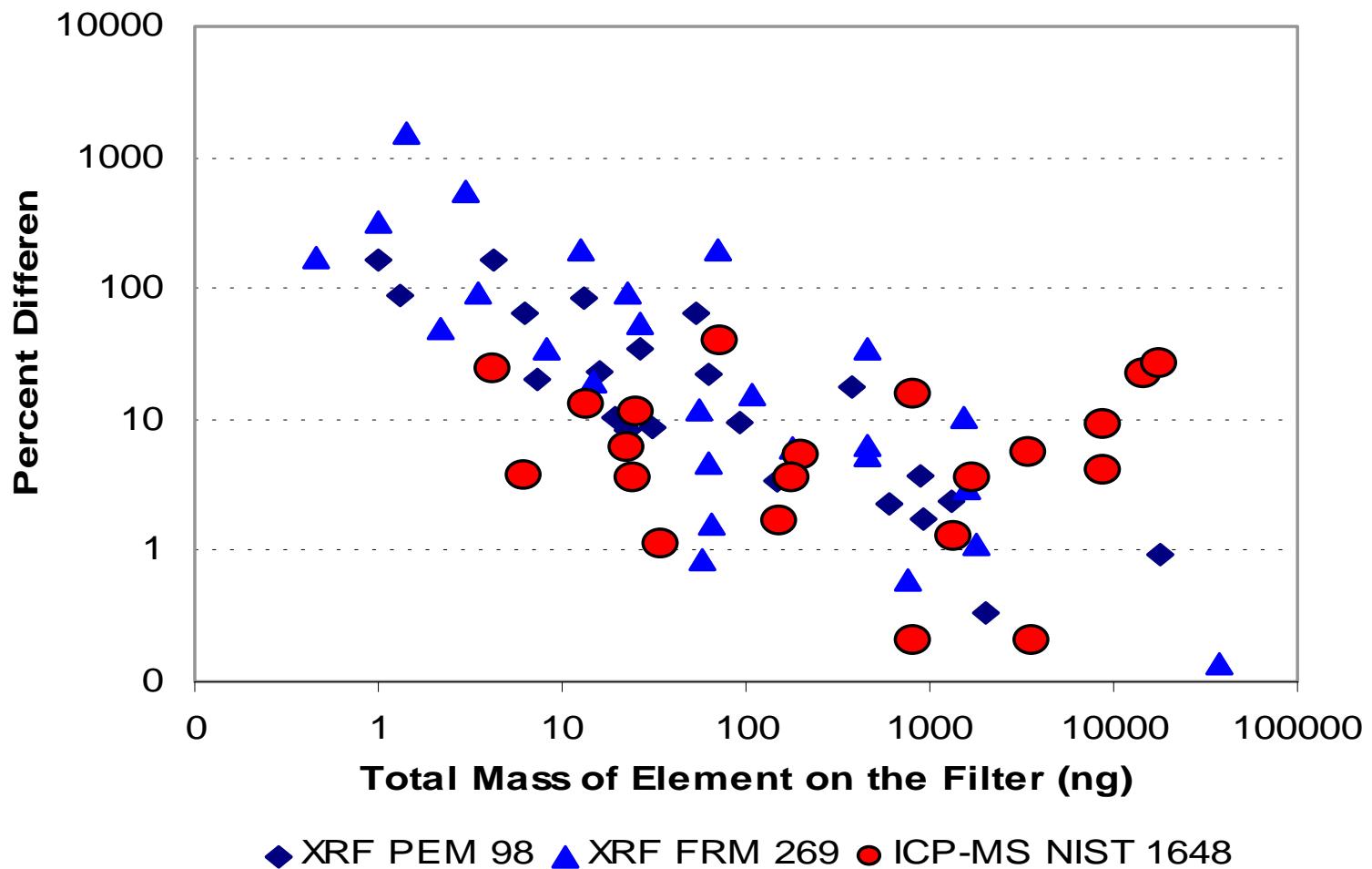


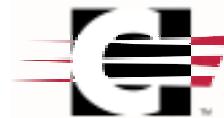
Comparison of XRF vs. DRC ICP-MS

- 15 sets of duplicate PM2.5 filters were generated with collocated FRM samplers
- 5 sets of duplicate PM2.5 filters were generated with collocated with Harvard multi-pollutant samplers (used for personal and indoor exposure program)
- 1 filter from each set analyzed by XRF and 1 filter analyzed by DRC ICP-MS
- NIST SRMs
- Investigate precision, accuracy, and results for collocated filters

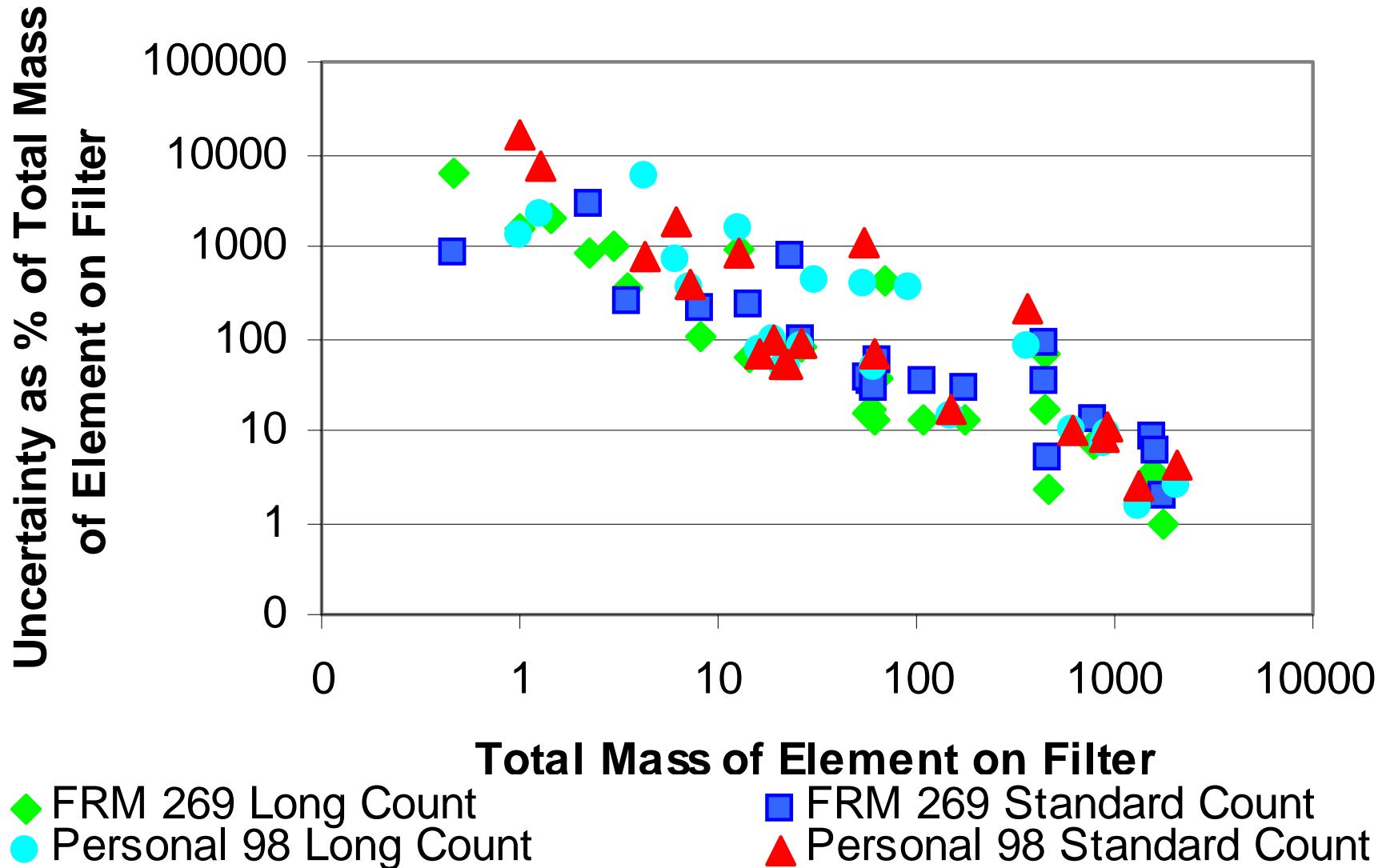


Precision Comparison of XRF vs. DRC ICP-MS





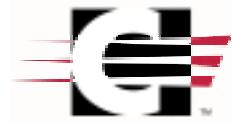
Precision of XRF



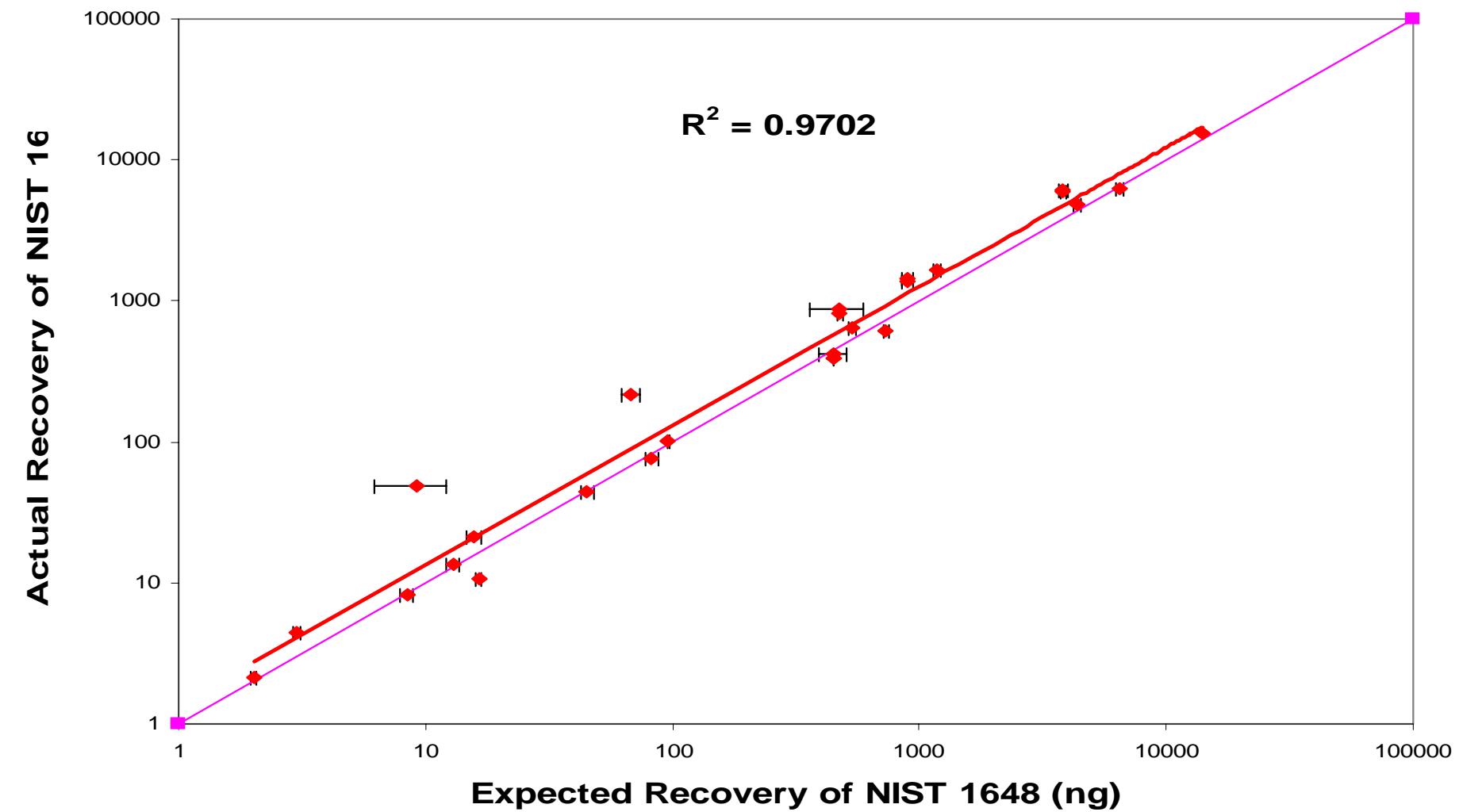


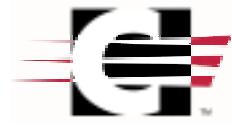
Accuracy Comparison of XRF vs. DRC ICP-MS

- **DRC ICP-MS**
 - Urban Particulate NIST SRM 1648
 - Digest 100 µg spiked onto filter inside a plastic vessel in hot block
 - Nitric/Hydrochloric/Hydrofluoric acids
 - HF complexed with clean Boric acid
 - NIST SRM 1643D diluted 1 to 10 (evaluate water soluble leach)
- **XRF**
 - No “SRMs” to evaluate.

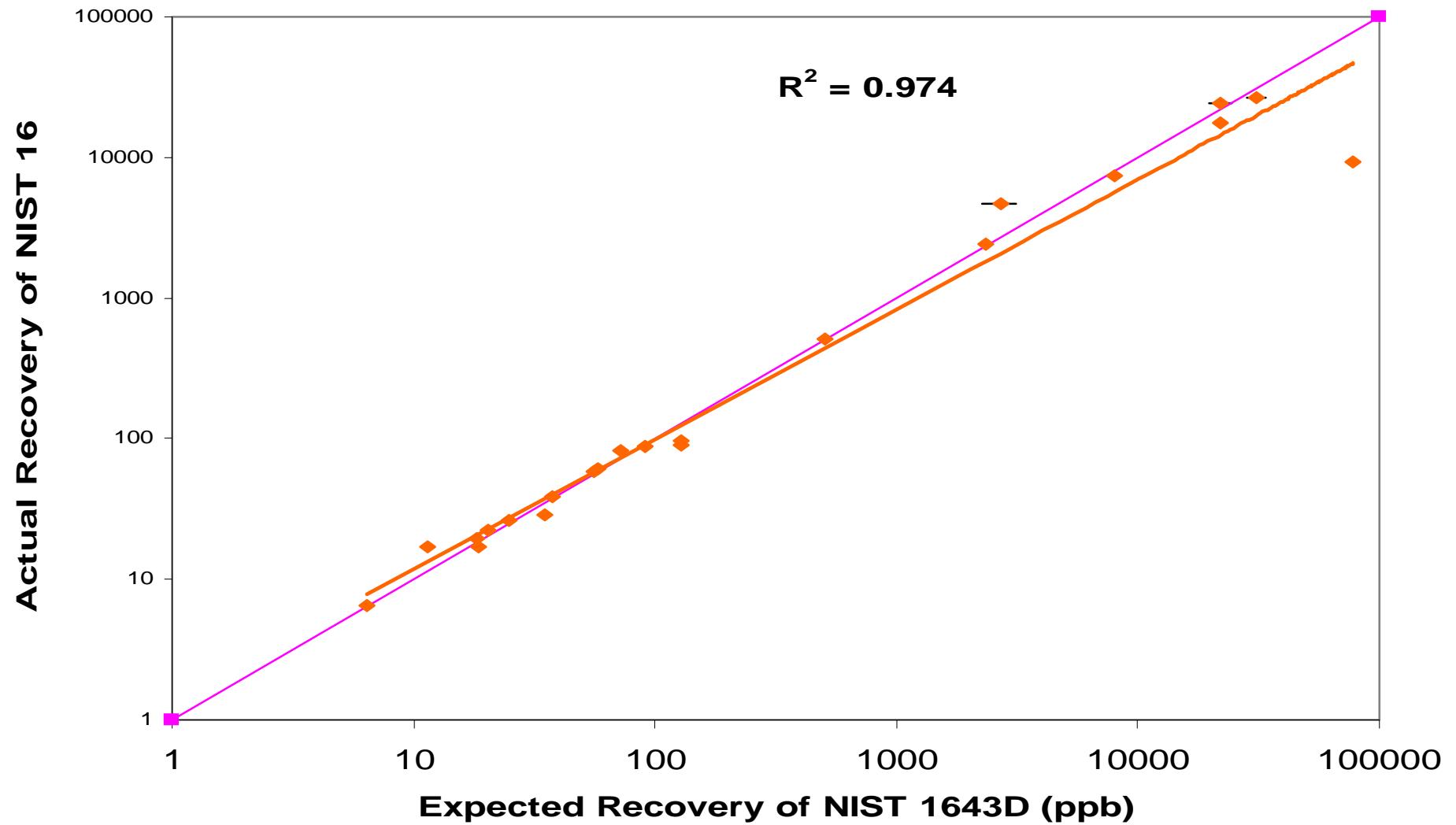


Accuracy of DRC ICP-MS





Accuracy of DRC ICP-MS





Comparison of XRF vs. DRC ICP-MS Duplicate Filters

Element Isotope	FILTERS 265 & 99021				FILTERS 260 & 99010				FILTERS 99008 & 259			
	Filter 265		Filter 99021		Filter 260		Filter 99010		Filter 99008		Filter 259	
	X-ray	ICP-MS	Concentration and Uncertainty	Concentration and Uncertainty	X-ray	ICP-MS	Concentration and Uncertainty	Concentration and Uncertainty	X-ray	ICP-MS	Concentration and Uncertainty	Concentration and Uncertainty
Filter Wt (mg)	0.368	0.368	0.349	0.349	0.786	0.786	0.82	0.82	0.42	0.42	0.432	0.432
Ca 40	462	27	605	20	1432	39	3298	112	1766	39	3317	171
Ca 44	462	27	1512	168	1432	39	3751	513	1766	39	2501	257
K 39	595	27	1447	98	2794	47	4577	239	1787	39	1898	185
Al 27	581	79	1224	26	5556	103	106626	27904	4847	81	59352	20114
Cr 50	22.4	26.8	17.6	2	14.7	29	44.5	3	35.4	10	23.2	1
Mn 55	56.7	7.6	68.7	3.8	57.1	8.3	93.9	3.5	78.3	8.7	87.2	0.8
Se 80	94.2	5.3	76.8	1.2	2165	16	1886	60	2625	18	2171	24
Fe 56	1038	13.9	1252	19	2511	21	3663	94	2827	22	3521	124
Na 23	652	786	1024	36	1084	0	3084	617	891	256	2789	523
Mg 24	285	362	215	11	0	532	1118	83	0	445	653	50
Si 28	1226	66	7995	2697	5556	103	76203	7041	4847	81	51892	2641
V 51	26.9	116	25.0	0.73	68.1	120	65.3	2.0	0	122	20.5	0.2
Ti 48	49.9	284	53.3	1.7	234	292	344	5.9	288	300	144	6.5
Cu 63	41.5	5	120	5.9	41.6	5.4	201	3.9	68.6	5.7	208	7.3
Co 59	4	22.1	1.4	0.13	0	43	77.6	1.2	0	48	4.6	0.2
Ni 60	13.8	4.5	40.5	1.9	17.4	5	64.8	3.2	13.2	15.1	29.1	2.0
Zn 66	275	6.6	495	23	308	7.1	412	25	543	8.4	604	14
As 75	19	33.6	26.3	1	0	121	75.7	3.6	0	212	54.8	2.9
Cd 111	46.4	124	6.8	0.62	84	130	4.7	0.3	0	134	12.2	0.8
Cd 114	46.4	124	9.2	0.49	84	130	3.8	0.2	0	134	11.1	0.6
Sn 118	0	178	14.2	0.83	0	186	41.1	0.5	11.9	188	44.0	1.1
Sn 120	0	178	13.7	1.9	0	186	38.9	3.1	11.9	188	43.6	1.6
Ba 135	0	705	25.8	3.7	0	736	80.0	6.5	0	758	78.3	5.2
Pb 208	105	13.4	97.8	2	151	188	188	3.4	624	76	689	24



Comparison of XRF vs. DRC Cell ICP-MS Duplicate Filters

XRF

- Sensitivity better than 20% uncertainty for only 7 elements.....Ca, K, Al, Fe, Si, Zn, and Pb
 - All other elements 20 - 1000%

DRC ICP-MS

- Sensitivity better than 20% uncertainty for all elements except Si
 - Si occasionally exceeded 20%



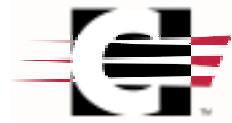
Comparison of XRF vs. DRC Cell ICP-MS Duplicate Filters

- Agreement/Non-Agreement
 - Within 20% for Pb, Se
 - Within 30% for Fe, Mn
 - Within 30-70% for Ca, K, Zn
 - 5 to 10 X difference for Si

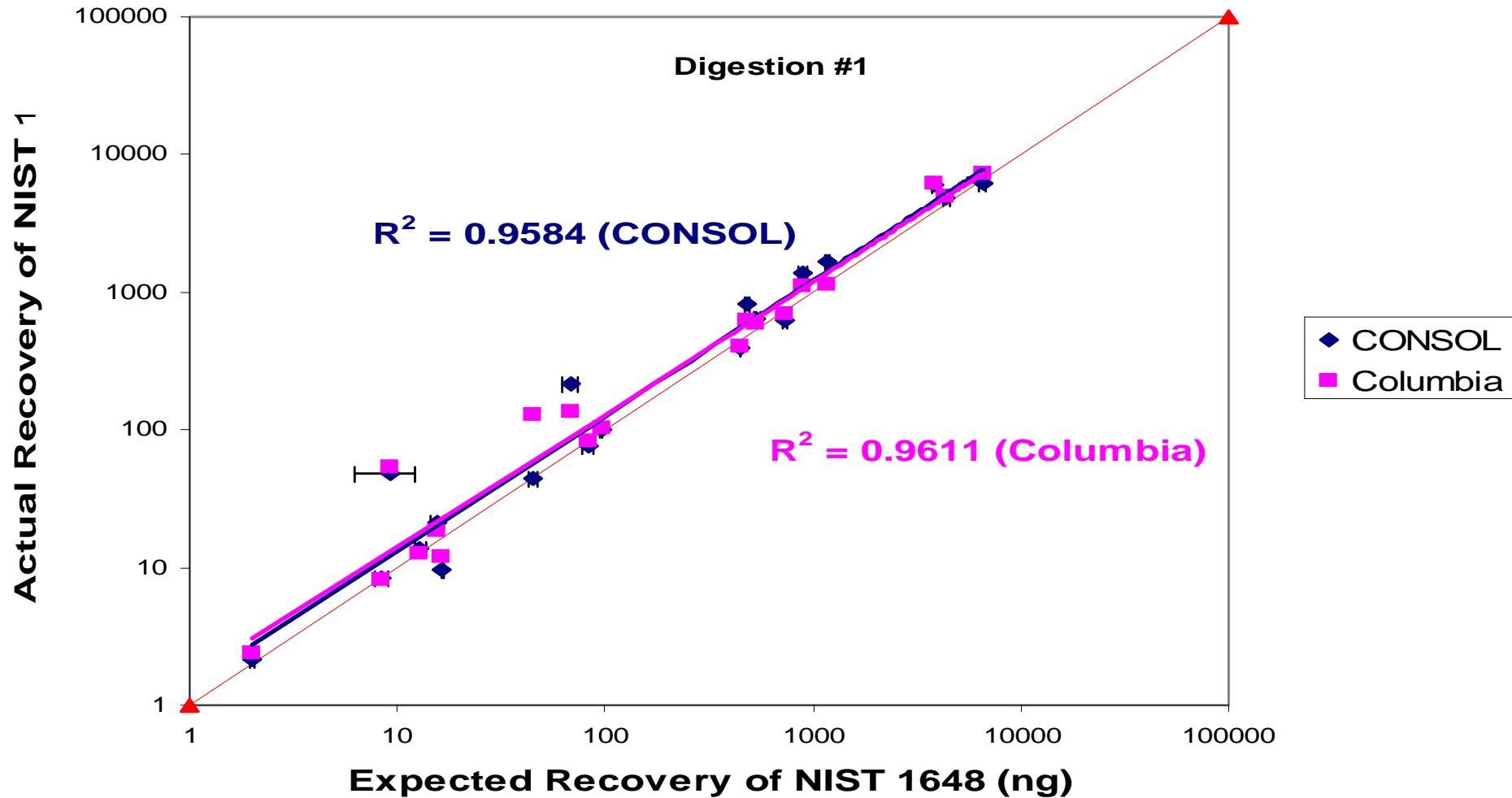


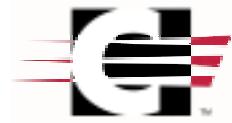
Additional Validation

- Select a referee technique – different method of resolving analyte from interferences
- Chose High Resolution ICP-MS
- Columbia University
- No other single technique could provide detection limits to DRC ICP-MS for all elements of interest

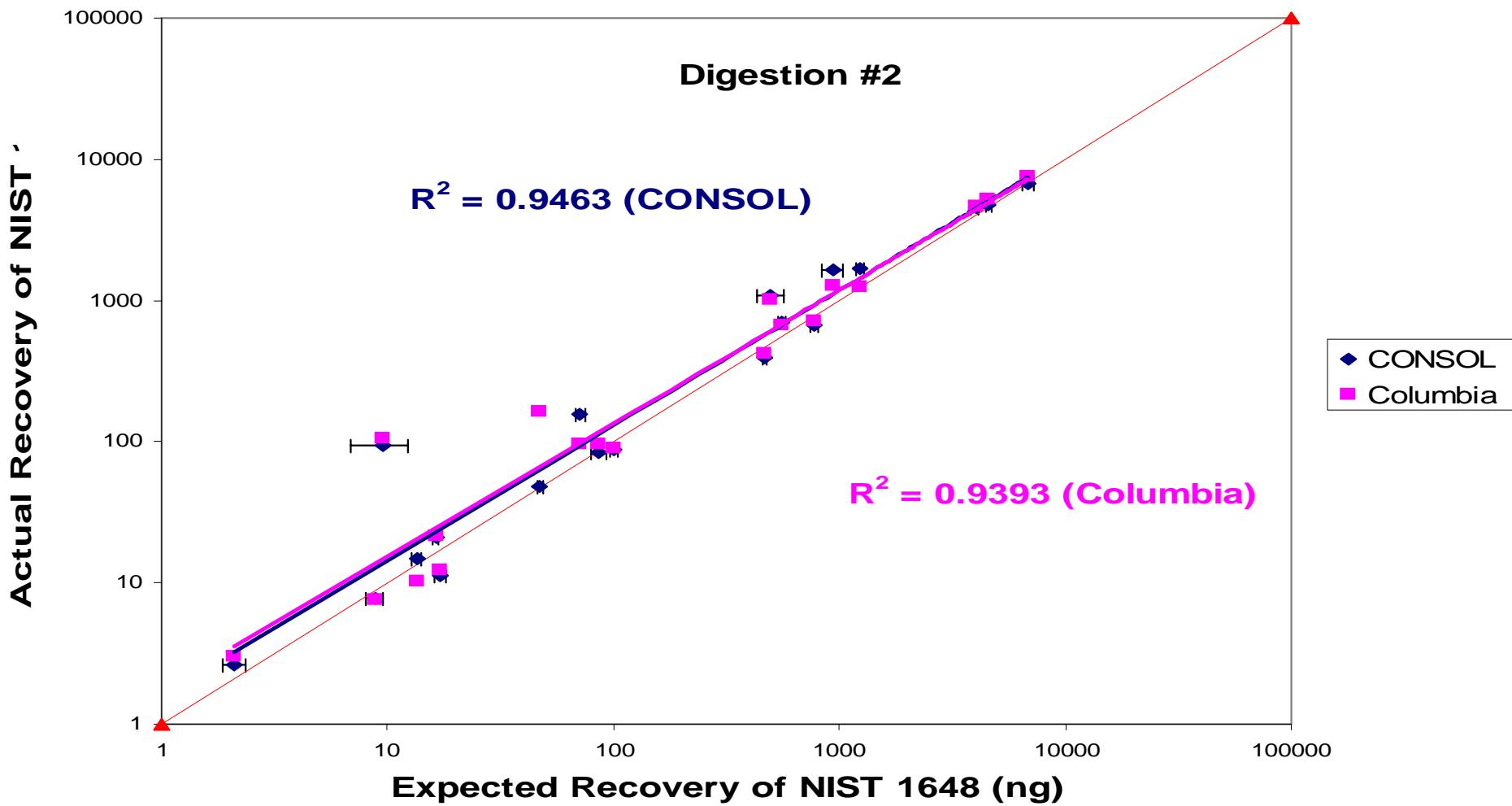


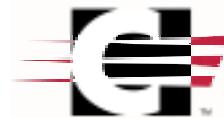
Accuracy Comparison of DRC ICP-MS vs. High Resolution ICP-MS





Accuracy Comparison of DRC ICP-MS vs. High Resolution ICP-MS





Comparison of XRF vs. DRC ICP-MS vs. High Resolution ICP-MS

Element	Isotope	COLOCATED FILTERS 92 & BCH 094 PM								COLOCATED FILTERS 98 & BCH 101 PM							
		Filter 92		Filter BCH 094 PM		Filter 98		Filter BCH 101 PM		Filter 92		Filter BCH 094 PM		Filter 98		Filter BCH 101 PM	
		DRI	DRI	CONSOL	CONSOL Columbia	DRI	DRI	CONSOL	CONSOL Columbia	DRI	DRI	CONSOL	CONSOL Columbia	DRI	DRI	CONSOL	CONSOL Columbia
Filter(mg)		0.213	0.213	0.213	0.213	0.167	0.167	0.167	0.167	0.167	0.167	0.167	0.167	0.167	0.167	0.167	0.167
Ca	40	885	++	25	2551	++	16.4	2757	915	++	25	1435	++	33	1557		
Ca	44	885	++	25	2988	++	200	915	++	25	1997	++	129				
K	39	521	++	21	1186	++	54	548	633	++	22	1326	++	84	723		
Al	27	554	++	48	1234	++	41.2	1019	963	++	48	2001	++	51	1614		
Cr	50	8.2	++	29	18.8	++	1.1	59.1	5.8	++	29.3	23.4	++	1.9	77.5		
Mn	55	44.4	++	8.6	106	++	1.4	97.8	50.7	++	8.7	72.5	++	4.9	69.3		
Se	80	10	++	11.1	17.0	++	0.37		20.1	++	3.7	23.7	++	0.78			
Fe	56	1318	++	13.4	2149	++	48.3	2001	1307	++	13	1810	++	74	1783		
Na	23	10.4	++	476	777	++	57.3	547	311	++	433	1667	++	43	1508		
Mg	24	87.3	++	219	408	++	18.7	292	76	++	200	515	++	32	386		
Si	28	923	++	41	9114	++	3031		2063	++	45	8100	++	1614			
Ti	48	65.9	++	225	120	++	2.5	103	108	++	226	150	++	3	149		
V	51	39.8	++	94.6	44.8	++	3.1	42.6	30.2	++	95.2	48.5	++	2.1	42.8		
Na	23	10.4	++	476	846	++	94.7	547.4	311.0	++	433.0	1858.3	++	139.0	1507.7		
Al	27	554	++	48.2	1241	++	46	1019.2	963.0	++	48.0	2020.7	++	53.0	1614.2		
Mg	24	87.3	++	219	428	++	28.2	381.2	75.6	++	200.0	560.0	++	10.0	534.1		
Ti	48	65.9	++	225	115	++	2.6	103.1	108.0	++	226.0	153.7	++	5.1	149.2		
Cu	63	7	++	17.6	33.9	++	1.1	19.7	10.2	++	18.0	56.0	++	0.7	34.8		
Cu								18.9							34.1		
Co	59	0	++	26.7	2.0	++	0.25	1.6	0.0	++	26.7	2.6	++	0.3	2.2		
Ni	60	20.2	++	5.5	50.9	++	1.6	45.8	24.2	++	5.6	59.8	++	2.8	56.1		
Zn	66	428	++	7.9	659	++	21.2	536	145	++	7	345	++	11	265		
Zn								570							253		
As	75	0.8	++	21.9	9.6	++	1.3	3.66	0.5	++	20.6	8.8	++	0.2	2.59		
As								3.09							1.70		
Cd	111	0	++	97.8	2.4	++	0.11	1.72	0	++	97.7	2.1	++	0.4	1.29		
Cd	114	0	++	97.8	4.5	++	0.27		0	++	97.7	4.1	++	0.2			
Sn	118	55.7	++	138	5.1	++	0.77	6.94	41.3	++	139	2.8	++	0.3	4.72		
Sn	120	55.7	++	138	33.7	++	49	6.94	41.3	++	139	3.2	++	1.2	4.72		
Ba	135	28.4	++	566	40.1	++	2.5	38.32	0	++	568	22.0	++	1.7	24.50		
Pb	208	56.1	++	9.8	55.3	++	3	46.13	42	++	9.5	52.4	++	1.4	43.69		



Summary of XRF vs. DRC ICP-MS vs. High Resolution ICP-MS

Element	XRF	High Resolution ICP-MS	DRC ICP-MS
Ca	Acceptable	Acceptable	Acceptable
K	Acceptable	Acceptable	Unacceptable
Al	Unacceptable	Acceptable	Acceptable
Cr	Unacceptable	Unacceptable	Acceptable
Mn	Unacceptable	Acceptable	Acceptable
Se	Acceptable	Acceptable	Acceptable
Fe	Acceptable	Acceptable	Acceptable
Na	Unacceptable	Unacceptable	Unacceptable
Mg	Unacceptable	Unacceptable	Unacceptable
Si	Unacceptable	Unacceptable	Acceptable
Ti	Unacceptable	Acceptable	Acceptable
V	Unacceptable	Acceptable	Acceptable
Cu	Unacceptable	Unacceptable	Unacceptable
Co	Unacceptable	Acceptable	Acceptable
Ni	Unacceptable	Unacceptable	Unacceptable
Zn	Acceptable	Acceptable	Acceptable
As	Unacceptable	Unacceptable	Unacceptable
Cd,	Unacceptable	Acceptable	Acceptable
Sn	Unacceptable	Acceptable	Acceptable
Ba	Unacceptable	Acceptable	Acceptable
Pb	Acceptable	Acceptable	Acceptable

Unacceptable Caution Acceptable



Conclusions

- XRF has adequate sensitivity to determine Ca, K, Al, Fe, Si, Zn, and Pb in PM_{2.5} filter particulate. DRC ICP-MS displays adequate sensitivity to determine all 21 elements of interest, however, analytical uncertainty for Si occasionally exceeds 20%.
- XRF and DRC ICP-MS results consistently agree within 20% for only Se and Pb. Results for Fe and Mn generally agree within 30%. Agreement is typically 30%-70% for Ca, Zn, K and Al. Si concentrations differ by a factor of 5-10. XRF concentrations are lower than DRC ICP-MS concentrations in almost all instances.
- DRC ICP-MS results for a NIST Urban Particulate and a NIST Water are generally in good agreement with reported values. Exceptions seem to be caused by background contamination of the sample during dissolution.



Conclusions

- Cost of analyzing a fine particulate sample by DRC ICP-MS is about the same as analyzing the sample by XRF. Consequently, DRC ICP-MS is a cost effective means of providing elemental results for the large number of filters produced by fine particulate programs.
- Results from the DRC ICP-MS compared to a High Resolution ICP-MS are generally in good agreement. Since High Resolution ICP-MS uses a different technique to resolve interferences, this suggests that the accuracy of the ICP-MS techniques are superior to the accuracy of the XRF.
- ICP-MS results for NIST standards are in general agreement with accepted concentrations.